

$\text{Me}_2\text{NHBH}_2\text{NMe}_2\text{BH}_3$ , the nitrogen base site in the parent aminoarsine effectively competes for the  $\text{BH}_3$  bound in the diborazane. This competition leads to dissociation of the diborazane and formation of a  $\text{BH}_3$  adduct of the aminoarsine.  $[\text{Me}_2\text{NBH}_2]_2$  forms and  $\text{BH}_3$ /aminoarsine adduct decomposition yields  $(\text{Me}_2\text{N})_2\text{BH}$  and an alternate route to the As-As-bonded products. These results are consistent with those obtained from our study of the analogous  $\text{BH}_3$ /aminoarsine systems with varying stoichiometry.<sup>3</sup>

### Experimental Section

**General Data.** Due to the nature of the materials, standard high-vacuum-line techniques and a nitrogen-filled dri-lab (Vacuum Atmospheres Model HE-43 Dri-Lab equipped with a Model HE-493 Dri-Train) were used for the storage and manipulation of all compounds.  $\text{Me}_2\text{AsNMe}_2$  (74 °C/108 mmHg),  $\text{MeAs}(\text{NMe}_2)_2$  (63 °C/50 mmHg), and  $\text{As}(\text{NMe}_2)_3$  (55–57 °C/10 mmHg) were synthesized by the reaction of  $\text{Me}_2\text{AsCl}$ ,  $\text{MeAsCl}_2$ , and  $\text{AsCl}_3$ , respectively, with a stoichiometric excess of  $\text{Me}_2\text{NH}$ .<sup>19</sup>  $\text{Me}_2\text{AsCl}$  (106 °C)<sup>20</sup> and  $\text{MeAsCl}_2$  (61–63 °C/50 mmHg)<sup>21</sup> were synthesized by previously reported methods. The aminoarsines were purified by distillation on a spinning-band column, and their purity was checked by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.  $\mu\text{-Me}_2\text{NB}_2\text{H}_3$  was synthesized by the procedure described by Spielman.<sup>5</sup> Toluene- $d_6$  was purchased from Wilmad Glass Co. and stored over molecular sieves.  $^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{13}\text{C}$  NMR spectra were recorded on a GE (Nicolet) 300-MHz multinuclear FT NMR spectrometer operating at 300.1, 96.3, and 75.4 MHz, respectively.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts were measured with respect to  $\text{Me}_4\text{Si}$  as an internal reference. The  $^{11}\text{B}$  NMR chemical shifts were measured relative to the signal of  $\text{BF}_3\cdot\text{OEt}_2$ , high-field shifts being taken as negative. The  $^{11}\text{B}$  and  $^{13}\text{C}$  NMR spectra were obtained under broadband  $^1\text{H}$  decoupling. Thus, all  $^{11}\text{B}$  and  $^{13}\text{C}$  NMR resonances were observed as singlets. Additionally, some  $^{11}\text{B}$  NMR spectra were obtained under coupled conditions to determine the magnitude of  $^1J(\text{BH})$ . NMR spectral data were independently determined in this laboratory in toluene- $d_6$  solution on prepurified or synthesized compounds identified in the reaction mixtures. The NMR data for all the adducts and prepurified or synthesized compounds are given in Table I.

**General Reaction of  $\mu\text{-Me}_2\text{NB}_2\text{H}_3$  with Aminoarsines.** J. Young VNMR tubes were charged with 1 mmol of the aminoarsine in 3.0 mL of toluene- $d_6$ , attached to the vacuum line, cooled to -115 °C (liquid-nitrogen/ethanol slush), and degassed. The vapor of  $\mu\text{-Me}_2\text{NB}_2\text{H}_3$  were treated as an ideal gas, and the appropriately measured amount of  $\mu\text{-Me}_2\text{NB}_2\text{H}_3$  was condensed onto the toluene solution. The sealed NMR tube was gently agitated and inserted into the precooled (-95 °C) probe of the spectrometer. The reactions were followed at 10-deg temperature intervals (-95 to +25 °C) by  $^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{13}\text{C}$  NMR spectroscopy.

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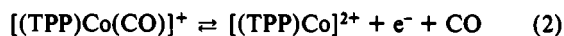
### Electrochemistry of (Octaethylporphyrinato)cobalt(II), (OEP)Co, under a Carbon Monoxide Atmosphere. Electrogeneration and Characterization of [(OEP)Co<sup>III</sup>(CO)]<sup>+</sup>

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The first example for carbon monoxide binding to a singly oxidized cobalt porphyrin was recently reported.<sup>1</sup> The investigated complex was [(TPP)Co(CO)]<sup>+</sup> (where TPP = the dianion of tetraphenylporphyrin), which was electrogenerated from (TPP)Co by cyclic voltammetry in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) under a CO atmosphere and characterized by thin-layer spectroelectrochemistry. Under these solution conditions, the initial Co(II) derivative undergoes three

oxidations, which are represented as shown in eqs 1–3.



The UV-visible spectrum of [(TPP)Co(CO)]<sup>+</sup> has bands at 431, 545, and 582 nm. An identical spectrum was obtained for electrogenerated [(TPP)Co(CH<sub>3</sub>CN)]<sup>+</sup> in  $\text{CH}_3\text{CN}$ , and on the basis of this similarity, a Co(III) oxidation state was assigned for the carbon monoxide complex.<sup>1</sup> However, a CO vibration band of [(TPP)Co(CO)]<sup>+</sup> was not reported nor was a diagnostic  $\pi$ -cation-radical marker band of singly or doubly oxidized (TPP)Co under CO presented.

Infrared  $\pi$ -cation-radical bands have been reported at 1290  $\text{cm}^{-1}$  for (TPP)Co(SbCl<sub>6</sub>)<sup>2-</sup> and at 1298  $\text{cm}^{-1}$  for electrogenerated [(TPP)Co]<sup>2+</sup> in  $\text{CH}_2\text{Cl}_2$ , 0.1 M TBAP.<sup>3</sup> The (TPP)Co(SbCl<sub>6</sub>)<sup>2-</sup> sample appears to be Co(II)  $\pi$  cation radical, but both electrochemically<sup>3,4</sup> and photochemically<sup>5</sup> generated [(TPP)Co]<sup>+</sup> seem to contain a Co(III) central metal ion in solutions of  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_2\text{Br}_2$ , or other chlorinated solvents. Under these solution conditions, a  $\pi$ -cation-radical band would thus be expected to appear upon oxidation of [(TPP)Co(CO)]<sup>+</sup> to [(TPP)Co<sup>III</sup>]<sup>2+</sup> (eq 2). However, this band would be difficult to observe, since the second and third oxidations of (TPP)Co are virtually overlapped in potential under a CO atmosphere<sup>1</sup> and this results in a direct conversion of [(TPP)Co(CO)]<sup>+</sup> to [(TPP)Co]<sup>3+</sup>, the latter of which is a Co(III) dication.

Octaethylporphyrin (OEP)  $\pi$ -cation-radical marker bands occur between 1540 and 1570  $\text{cm}^{-1}$  in the infrared region<sup>2,6–8</sup> and are easily observed in  $\text{CH}_2\text{Cl}_2$  solutions containing TBAP as supporting electrolyte.<sup>8</sup> Three stable, oxidized species can be stepwise generated from (OEP)Co in  $\text{CH}_2\text{Cl}_2$  under CO, and each is characterized in this paper by UV-visible and FTIR spectroelectrochemistry. The resulting data are self-consistent and provide the first conclusive evidence for the formation of a [(OEP)Co<sup>III</sup>(CO)]<sup>+</sup> complex in solution.

### Experimental Section

**Instrumentation and Procedure.** Cyclic voltammograms were obtained with a PAR Model 273 potentiostat and an Omnigraphic 2000 X-Y recorder. A platinum button electrode with a surface area of 0.8  $\text{mm}^2$  was used as the working electrode. A homemade aqueous saturated calomel electrode (SCE) was used as the reference electrode and was separated from the bulk solution by a salt bridge filled with  $\text{CH}_2\text{Cl}_2$  and 0.2 M tetrabutylammonium perchlorate (TBAP). A large surface area platinum electrode served as the auxiliary electrode.

A Matheson Model 8250 modular Dyna-Blender with flowmeter was used to deliver carbon monoxide/nitrogen mixtures that contained between 1 and 100% CO. The vapor pressure of methylene chloride (382 mmHg at 23 °C) was subtracted from the total pressure in calculating the partial pressure of CO.

In situ FTIR measurements were carried out with a light transparent spectroelectrochemical cell<sup>9</sup> by using an IBM IR32 spectrometer with an IBM 9000 computer system. The spectrum containing 0.2 M TBAP was taken as background to minimize matrix interferences.

UV-visible spectroelectrochemistry was carried out with a vacuum-tight thin-layer spectroelectrochemical cell that had a doublet platinum gauze working electrode.<sup>10</sup> A Tracor Northern TN-6500 multichannel analyzer was used for obtaining thin-layer UV-visible spectra.

High-purity  $\text{N}_2$  was used to deoxygenate the solution before each experiment. All potentials are reported vs a saturated calomel electrode (SCE).

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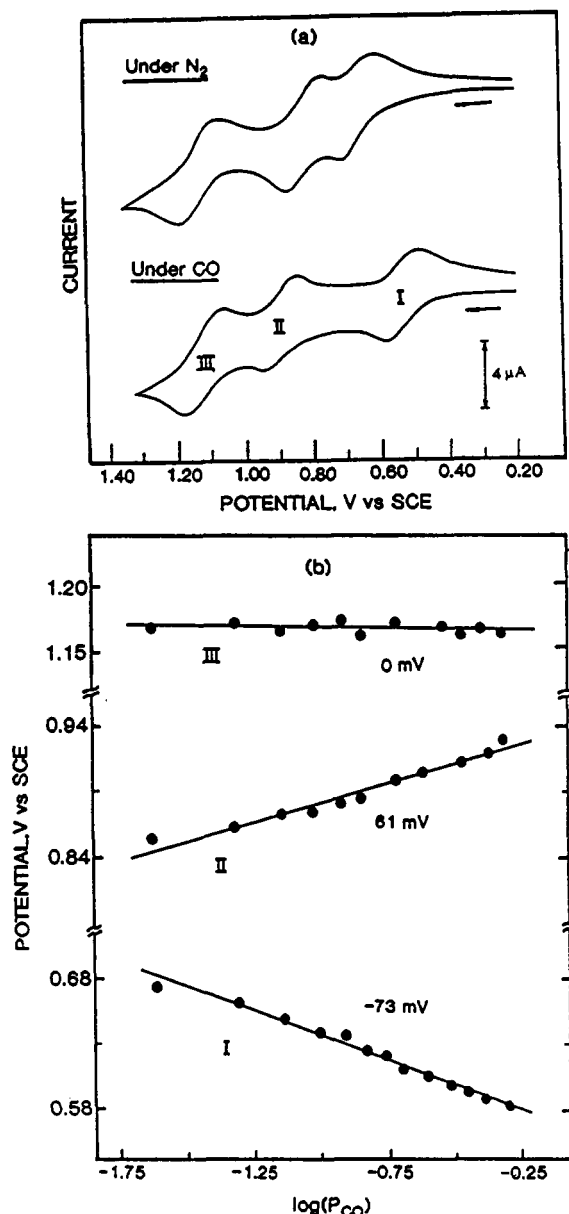
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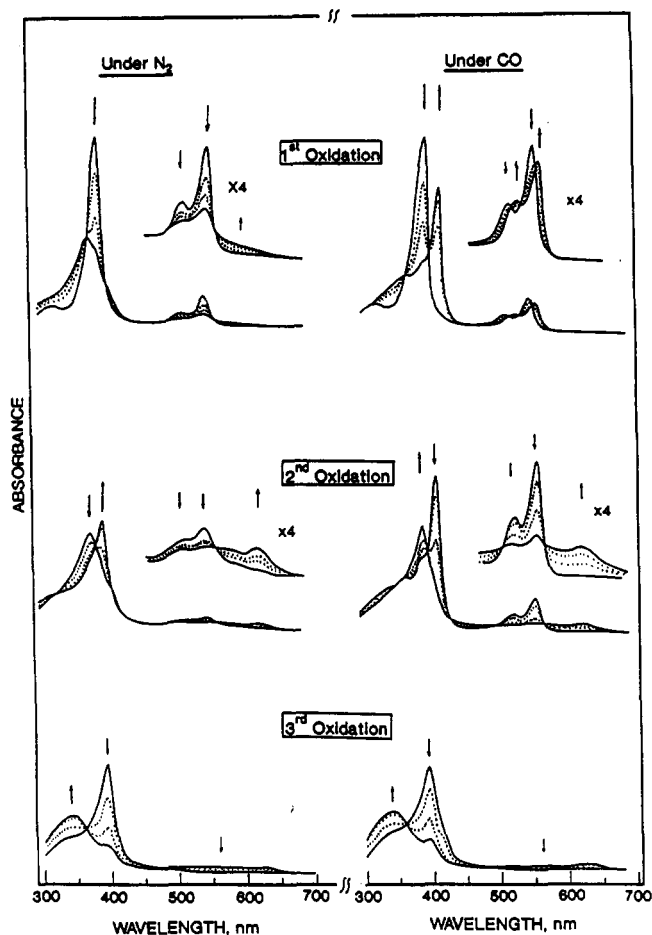
**Figure 1.** (a) Cyclic voltammograms for oxidation of 2.0 mM (OEP)Co in  $\text{CH}_2\text{Cl}_2$  containing 0.2 M TBAP under  $\text{CO}$  or  $\text{N}_2$  atmospheres and (b) plot of  $E_{1/2}$  for each electrode reaction as a function of the  $\text{CO}$  partial pressure in a  $\text{CO}/\text{N}_2$  mixture of 1-atm total pressure. The three oxidations under a  $\text{CO}/\text{N}_2$  mixture are labeled as reactions I–III.

**Chemicals.** (OEP)Co was prepared according to published methods<sup>11</sup> and was generously provided by Dr. C. K. Chang. Methylene chloride ( $\text{CH}_2\text{Cl}_2$ , spectroanalyzed grade) was obtained from Fisher Scientific Co. and was freshly distilled from  $\text{CaH}_2$  before use. Tetra-*n*-butylammonium perchlorate was purchased from Fluka Chemical Co., recrystallized from absolute ethanol, and dried in a vacuum oven at 40 °C prior to use. CP grade carbon monoxide ( $\text{CO}$ ) was obtained from Union Carbide Corp., Linde Division.

### Results

Cyclic voltammograms for the oxidation of (OEP)Co in  $\text{CH}_2\text{Cl}_2$  under  $\text{N}_2$  and  $\text{CO}$  atmospheres are illustrated in Figure 1, which also shows how  $E_{1/2}$  for each electrode reaction varies as a function of the  $\text{CO}$  partial pressure in  $\text{CH}_2\text{Cl}_2$  under a  $\text{CO}/\text{N}_2$  gas mixture.

The UV-visible changes were monitored during each one-electron oxidation under  $\text{N}_2$  or  $\text{CO}$ , and the resulting thin-layer spectra are shown in Figure 2. Values of  $\lambda$  and  $\epsilon$  for each of the electrooxidized species are summarized in Table I. FTIR difference spectra of singly and doubly oxidized (OEP)Co were also



**Figure 2.** Thin-layer UV-visible spectra obtained during controlled-potential oxidation of 0.2 mM (OEP)Co in  $\text{CH}_2\text{Cl}_2$  containing 0.2 M TBAP.

**Table I.** Half-Wave Potentials (V vs SCE) and Spectral Characteristics of Neutral and Electrooxidized (OEP)Co in  $\text{CH}_2\text{Cl}_2$  Containing 0.2 M TBAP under a  $\text{N}_2$  or  $\text{CO}$  Atmosphere

electrode reacn	atmosphere	$E_{1/2}$	$\lambda_{\text{max}}$ , nm ( $10^{-4}\epsilon$ , $\text{cm}^{-1}\text{M}^{-1}$ )		
none <sup>a</sup>	$\text{N}_2$		392 (2.4)	517 (0.3)	551 (0.5)
	$\text{CO}$		392 (2.4)	517 (0.3)	551 (0.5)
1st oxidn <sup>b</sup>	$\text{N}_2$	0.67	377 (1.2)	517 (0.2)	551 (0.3)
	$\text{CO}$	0.58	412 (1.8)	529 (0.3)	560 (0.4)
2nd oxidn <sup>b</sup>	$\text{N}_2$	0.85	395 (1.3)	627 (0.2)	
	$\text{CO}$	0.93	395 (1.2)	627 (0.2)	
3rd oxidn <sup>b</sup>	$\text{N}_2$	1.17	346 (0.7)	655 (0.2)	
	$\text{CO}$	1.17	346 (0.7)	655 (0.2)	

<sup>a</sup>Original compound. <sup>b</sup>See cyclic voltammograms in Figure 1.

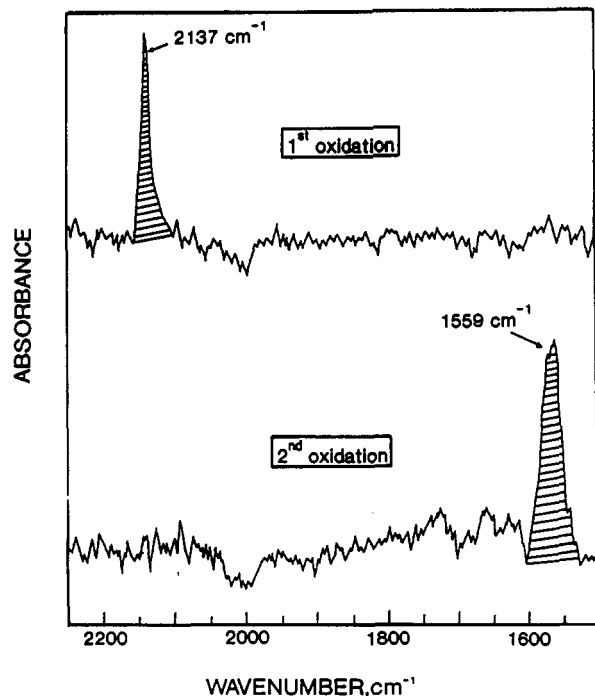
measured under a  $\text{CO}$  atmosphere, and the resulting spectra between 1550 and 2250  $\text{cm}^{-1}$  are shown in Figure 3.

### Discussion

The oxidation of (OEP)Co in nonaqueous media has been thoroughly studied by chemical<sup>12,13</sup> and electrochemical methods.<sup>14–16</sup> Three well-separated one-electron oxidations occur in

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**Figure 3.** FTIR difference spectra obtained after the first two oxidations of 2.0 mM (OEP)Co in CH<sub>2</sub>Cl<sub>2</sub>, 0.2 M TBAP under 1 atm of CO. The first oxidation was carried out at 0.75 V and the second at 1.05 V. Both spectra are presented as the difference between the spectra of the electrooxidized species and neutral (OEP)Co under the same experimental conditions.

CH<sub>2</sub>Cl<sub>2</sub> under a N<sub>2</sub> atmosphere and are located at  $E_{1/2} = 0.67$ , 0.85, and 1.17 V vs SCE. The first oxidation was initially assigned as a Co(II) → Co(III) transition,<sup>15</sup> but later infrared, Raman, and ENDOR studies indicated that a Co(II)  $\pi$  cation radical is generated in noncoordinating media.<sup>17-19</sup>

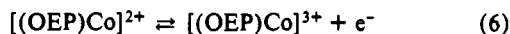
The first oxidation of (OEP)Co (reaction I) shifts by -73 mV per 10-fold increase in  $P_{CO}$ , and this value may be compared with a theoretical slope of -59 mV for the case where one CO molecule is complexed to the product of the first oxidation, as shown in eq 4.



The second oxidation (reaction II) shifts by +61 mV per 10-fold increase in  $P_{CO}$ , and this slope may be compared to a theoretical +59 mV slope that would be obtained for an electrode reaction in which the CO molecule dissociates to give [(OEP)Co]<sup>2+</sup>, as shown in eq 5.



$E_{1/2}$  for the third oxidation of (OEP)Co (reaction III) is independent of the CO partial pressure and is also identical with the value obtained under a N<sub>2</sub> atmosphere. This lack of dependence on CO partial pressure is consistent with the electrode reaction given in eq 6, and this was confirmed by thin-layer UV-visible and FTIR spectroelectrochemistry.



The initial UV-visible spectra of (OEP)Co are independent of the gas above the solution (see Table I), indicating that neither CO nor N<sub>2</sub> interacts with the neutral complex. However, large spectral differences exist in the product generated after abstraction of one electron from (OEP)Co. The singly oxidized complex under a N<sub>2</sub> atmosphere has a substantially decreased Soret band (located

at 377 nm) and a spectrum virtually identical with the one reported in the literature for [(OEP)Co]<sup>+</sup>Br<sup>-15,18</sup> or [(OEP)Co]<sup>+</sup>ClO<sub>4</sub><sup>-15,17,18</sup>. The latter two species have been characterized as Co(II)  $\pi$  cation radicals and have spectra that are quite different from the species generated after the abstraction of one electron from (OEP)Co under a CO atmosphere. This spectrum is shown in Figure 2 and has bands at 412, 529, and 560 nm. It resembles the spectrum of singly oxidized (OEP)Co in CH<sub>2</sub>Cl<sub>2</sub> containing methanol<sup>17</sup> or H<sub>2</sub>O<sup>18</sup> and is assigned as that of a genuine Co(III) complex, i.e. [(OEP)Co<sup>III</sup>(CO)]<sup>+</sup>.

The two one-electron oxidations of [(OEP)Co]<sup>+</sup> and [(OEP)Co(CO)]<sup>+</sup> give products that have identical UV-visible spectra under N<sub>2</sub> or CO (see Figure 2 and Table I). The UV-visible data are thus consistent with the electrochemical results, which indicate that CO binds only to the singly oxidized complex, and this was confirmed by in situ FTIR spectroelectrochemistry.

The first oxidation of (OEP)Co produces a species that has a strong IR band at 2137 cm<sup>-1</sup> and is assigned as the CO vibration of [(OEP)Co(CO)]<sup>+</sup>. There are no discernible  $\pi$ -cation-radical bands in the region of 1540-1570 cm<sup>-1</sup>. This contrasts with [(OEP)Co<sup>II</sup>]<sup>+</sup> under N<sub>2</sub>, which has a 1560-cm<sup>-1</sup> band and has been assigned as a Co(II)  $\pi$  cation radical.<sup>6,7</sup>

A strong 1559-cm<sup>-1</sup> band is present after controlled-potential oxidation of [(OEP)Co(CO)]<sup>+</sup> at 1.05 V (reaction II), and at the same time, there is a loss of the CO vibration (see Figure 3). These spectra indicate the generation of a porphyrin  $\pi$  cation radical only after loss of the CO axial ligand in the second oxidation. The  $\pi$ -cation-radical band disappears after the third oxidation of (OEP)Co, and an identical IR spectrum is obtained under CO or N<sub>2</sub> atmospheres. This agrees with the formation of a [(OEP)Co<sup>III</sup>]<sup>3+</sup> product, as shown by the electrochemical and UV-visible data presented earlier.

In summary, all of the spectroscopic and electrochemical data are consistent with the formation of [(OEP)Co<sup>III</sup>(CO)]<sup>+</sup> under a CO atmosphere. This compound has a well-defined Co(III) UV-visible spectrum and a strong CO vibration at 2137 cm<sup>-1</sup>. The only previously characterized [(OEP)M<sup>III</sup>(CO)]<sup>+</sup> complex is (OEP)Ir(CO)Cl, which has a 2056-cm<sup>-1</sup> vibration in CH<sub>2</sub>Cl<sub>2</sub> under N<sub>2</sub>.<sup>8</sup> The [(OEP)Co(CO)]<sup>+</sup> derivative is relatively stable in CH<sub>2</sub>Cl<sub>2</sub> under CO, but the carbon monoxide axial ligand is lost upon either reduction to give (OEP)Co<sup>II</sup> or oxidation to give [(OEP)Co<sup>III</sup>]<sup>2+</sup>.

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#### Syn and Anti Isomers of Pd<sub>2</sub>Cl<sub>2</sub>( $\mu$ -dpmMe)<sub>2</sub> (dpmMe = 1,1-Bis(diphenylphosphino)ethane)

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Bis(diphenylphosphino)methane (dpm) is one of the most extensively used bidentate, bridging ligands within homo- and heterobimetallic complexes.<sup>2</sup> Replacement of one of the methylene hydrogens by a methyl group yields 1,1-bis(diphenyl-

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